Patent Claims

Salts of saturated, partially or fully unsaturated, heterocyclic cations having 1. the bis(trifluoromethyl)imide anion, N(CF₃)₂, which have the general formula (1)

$$[(R^1)_n - X A]^+$$
 $[N(CF_3)_2]^-$ (1)

where

A =

X =N, P, O or S

10

5

an integer selected from 0, 1 or 2 in such a way that X is satun = rated in accordance with its valency increased by 1,

15

a saturated, partially or fully unsaturated 3- to 8-membered hydrocarbon chain,

> in which all carbon atoms apart from one may be replaced by identical or different heteroatoms selected from N, P, O and S, where the carbon atoms of the hydrocarbon chain and the heteroatoms present therein are saturated by substituents R2 in accor-

20

dance with their valency,

 $R^{1}. R^{2} =$ -H, with the proviso that there is no bond to the positively charged heteroatom.

25

straight-chain or branched alkyl having 1-20 carbon atoms straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds

straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds

30

saturated, partially or fully unsaturated cycloalkyl having 3-7 carbon atoms

5

10

15

20

- halogen, in particular fluorine or chlorine, with the proviso that, for X = N, O, S, there is no halogen-heteroatom bond,
- -NO₂, with the proviso that there is no bond to a positively charged heteroatom,
- -CN, with the proviso that there is no bond to a positively charged heteroatom.

where the R² and/or R¹ in different and/or identical position of the heterocyclic ring are in each case identical or different,

where the R² and/or R¹ may be connected to one another in pairs by a single or double bond,

where one or more R² and/or R¹ may be partially or fully substituted by halogens, in particular -F and/or -CI, or partially by -CN or -NO₂, with the proviso that not all R² and R¹ are fully halogenated,

and where one or two carbon atoms of the R¹ and/or R² may be replaced by heteroatoms and/or atomic groups selected from the group -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially or perfluorinated C₁- to C₆-alkyl or -C₆F₅, where the α -position of the R¹ is not replaced for X = O, S.

- 25 2. Salts according to Claim 1, in which A is a 4-, 5- or 6-membered hydrocarbon chain.
 - Salts according to Claim 1 or 2, in which A is a hydrocarbon chain in which zero, one or two carbon atoms are replaced by heteroatoms selected from N, P, O and S.
- 30 4. Salts according to one of Claims 1 to 3, in which R¹, R², independently of one another, have the meaning -H, with the proviso that there is no bond to the positively charged heteroatom,

halogen, in particular fluorine, with the proviso that for X = N, O, S, there is no halogen-heteroatom bond, straight-chain or branched alkyl having 1-6 carbon atoms, in particular -CH₃, -C₂H₅, -*n*-C₃H₇, -CH(CH₃)₂, -*n*-C₄H₉, -*n*-C₆H₁₃, straight-chain or branched, partially or perfluorinated alkyl having 1-6 carbon atoms, in particular -CF₃, -C₂F₅, -C₄F₉.

5. Salts according to one of Claims 1 to 4, in which the saturated, partially or fully unsaturated, heterocyclic cation is selected from the following group:

$$(R^{1})_{n}$$
 $(R^{2})_{m}$ $(R^{2})_{m}$

10 where

15

5

X = N, P, O or S

Y = in each case, independently of one another, N, P, O, S or C, where at least one Y = C

n = 0 for unsaturated X = O, S 1 for saturated X = O, S or for unsaturated X = N, P 2 for saturated X = N, P

m = 0 for saturated Y = O, S or for unsaturated Y = N, P 1 for saturated Y = N, P or for Y = sp²-C 2 for Y = sp³-C

where the radicals R¹, R² are as defined in Claim 1.

6. Salts according to one of Claims 1 to 4, in which the saturated, partially or fully unsaturated, heterocyclic cation is selected from the following group:

where

5

10

15

20

X = in each case, independently of one another, N, P, O, S or C, where at least one X = N, P, O or S

n = 0 for saturated X = O, S or for unsaturated X = N, P

1 for saturated X = N, P or for X = sp²-C

or for substitution on the sp² ring carbon atom

2 for X = sp³-C

or for substitution on the sp³ ring carbon atom

where n is increased by 1 for one X = N, P, O or S

A' = saturated, partially or fully unsaturated 2- to 7-membered hydrocarbon chain, where the carbon atoms of the hydrocarbon chain are saturated by substituents R² in accordance with their valency

where the radicals R^1 , R^2 are as defined in Claim 1, with the proviso that the substituents R^1 in the α -position to the positively charged heteroatom do not have a methylene group directly adjacent to the heterocyclic ring.

7. Salts according to one of Claims 1 to 4, in which the saturated, partially or fully unsaturated, heterocyclic cation has the following structure

WO 2004/054991 PCT/EP2003/012811
- 29 -

 $(R^1)_n$ \dot{Y} A

where

10

15

20

X = N or P

Y = N, P, O or S

> A' = saturated, partially or fully unsaturated 2- to 7-membered hydrocarbon chain,

> B' = saturated, partially or fully unsaturated 1- to 6-membered hydrocarbon chain,

where all carbon atoms of the hydrocarbon chains A' and B' apart from one may be replaced by identical or different heteroatoms selected from N, P, O and S

and where the carbon atoms of the hydrocarbon chains A' and B' are saturated by substituents R² in accordance with their valency

and where the radicals R^1 , R^2 are as defined in Claim 1.

8. Salts of saturated, partially or fully unsaturated, heterocyclic di-cations having the bis(trifluoromethyl)imide anion, N(CF₃)₂, which have the general formula (2)

$$\begin{bmatrix} (R^{1})_{n} - X & Y - (R^{3})_{m} \end{bmatrix}^{2+} 2 [N(CF_{3})_{2}]^{-} (2)$$

whei	re
------	----

X, Y =each, independently of one another, N, P, O or S an integer selected from 0, 1 or 2 in such a way that X and Y n, m =5 are each saturated in accordance with their valency increased by 1, A'', B'' =saturated, partially or fully unsaturated 0- to 4-membered hydrocarbon chain, in which the carbon atoms may be replaced by identical or dif-10 ferent heteroatoms selected from N, P, O and S, where at least one carbon atom is present in the chains A" and B" together and where the carbon atoms of the hydrocarbon chains A" and B" and the heteroatoms present therein are saturated by substitu-15 ents R² in accordance with their valency, R^1 , R^2 , $R^3 = -H$, with the proviso that there is no bond to the positively charged heteroatom, straight-chain or branched alkyl having 1-20 carbon atoms 20 straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds saturated, partially or fully unsaturated cycloalkyl having 3-7 25 carbon atoms halogen, in particular fluorine or chlorine, with the proviso that, for X, = N, O, S, there is no halogen-heteroatom bond, -NO₂, with the proviso that there is no bond to a positively 30 charged heteroatom, -CN, with the proviso that there is no bond to a positively charged heteroatom, where the R¹, R² and/or R³ in different and/or identical position of the heterocyclic ring are in each case identical or different, 35

5

10

15

where the R¹, R² and/or R³ may be connected to one another in pairs by a single or double bond,

where one or more R¹, R² and/or R³ may be partially or fully substituted by halogens, in particular -F and/or -CI, or partially by -CN or -NO₂, with the proviso that that not all R¹, R² and R³ are fully halogenated,

and where one or two carbon atoms of the R^1 , R^2 and/or R^3 may be replaced by heteroatoms and/or atomic groups selected from the group -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially or perfluorinated C_1 - to C_6 -alkyl or - C_6F_5 , where the α -positions of the R^1 and of the R^3 are not replaced for X = O, S or Y = O, S,

where the heterocyclic di-cation is a 4-, 5-, 6-, 7-, 8- or 9-membered ring.

- 9. Salts according to Claim 8, in which the heterocyclic di-cation is a 5-, 6- or 7-membered ring.
- 20 10. Salts of saturated, partially or fully unsaturated, heterocyclic cations having the bis(trifluoromethyl)imide anion, N(CF₃)₂, which have the general formula (3)

$$(R^{2})_{m}$$
 X
 Y
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$
 $(R^{2})_{m}$

where

25 X, Y = each, independently of one another, N, P, O or S

	n =	an integer selected from 0, 1 or 2 in such a way that X is saturated in accordance with its valency increased by 1,
5	m =	an integer selected from 0, 1 or 2 in such a way that Y is saturated in accordance with its valency,
	R^1 , $R^2 =$	heteroatom,
10		straight-chain or branched alkyl having 1-20 carbon atoms straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds
		straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds
15		saturated, partially or fully unsaturated cycloalkyl having 3-7 carbon atoms
		halogen, in particular chlorine, with the proviso that, for X, = N, O, S, there is no halogen-heteroatom bond,
		-OR, with the proviso that the substituted heteroatom is not O or S,
20		where the R ² and/or R ¹ in different and/or identical position of the heterocyclic ring are in each case identical or different,
		where the R ² and/or R ¹ may be connected to one another in pairs by a single or double bond,
25		where one or more R^2 and/or R^1 may be partially or fully substituted by halogens, in particular -F and/or -Cl, or partially by -CN or -NO ₂ , with the proviso that not all R^2 and R^1 are fully halogenated,
30		and where one or two carbon atoms of the R^1 and/or R^2 may be replaced by heteroatoms and/or atomic groups selected from the group -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO ₂ -, -SO ₂ O-, -N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially or perfluorinated C_1 - to C_6 -alkyl or - C_6 F ₅ , where the α -position of the R^1 is not
35		replaced for X = O, S.

11. Process for the preparation of salts according to one of Claims 1 to 7, characterised in that an alkali metal fluoride of the general formula DF, where D selected from the group of the alkali metals, is reacted in a polar organic solvent with

5 $R^FSO_2N(CF_3)_2$ or $R^FC(O)N(CF_3)_2$

where $R^F = F$ or C_pF_{2p+1} , where p = 1 - 8,

and a salt of the general formula (4)

$$\begin{bmatrix} (R^1)_n - X & A \end{bmatrix}^+ \quad E^- \quad (4)$$

where

10 E^- = F^- , CI^- , Br^- , I^- , BF_4^- , CIO_4^- , AsF_6^- , SbF_6^- , $SbCI_6^-$, PF_6^- , $R^FSO_3^-$, FSO_3^- , $(R^F)_2P(O)O^-$, $R^FP(O)_2O^-$, RSO_3^- , $ROSO_3^-$, $R^FC(O)O^-$, $RC(O)O^-$, $RC(O)O^$

phenolate, where R^F is a perfluorinated C_1 to C_8 -alkyl group or perfluorinated aryl group and R is a C_1 to C_8 -alkyl group or aryl

15 group

20

25

X = N, P, O or S

n = an integer selected from 0, 1 or 2 in such a way that X is satu-

rated in accordance with its valency increased by 1,

A = a saturated, partially or fully unsaturated 3- to 8-membered hydrocarbon chain,

dance with their valency,

in which all carbon atoms apart from one may be replaced by identical or different heteroatoms selected from N, P, O and S, where the carbon atoms of the hydrocarbon chain and the heteroatoms present therein are saturated by substituents R² in accor-

WO 2004/054991 PCT/EP2003/012811

		R^{1} , R^{2} =	-H, with the proviso that there is no bond to the positively charged heteroatom,
5			straight-chain or branched alkyl having 1-20 carbon atoms straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds
			straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds
10			saturated, partially or fully unsaturated cycloalkyl having 3-7 carbon atoms
			halogen, in particular fluorine or chlorine, with the proviso that, for X = N, O, S, there is no halogen-heteroatom bond,
			-NO ₂ , with the proviso that there is no bond to a positively charged heteroatom,
15			-CN, with the proviso that there is no bond to a positively charged heteroatom,
			where the R ² and/or R ¹ in different and/or identical position of the heterocyclic ring are in each case identical or different,
20			
			where the R ² and/or R ¹ may be connected to one another in pairs by a single or double bond,
			where one or more R ² and/or R ¹ may be partially or fully substi-
25			tuted by halogens, in particular -F and/or -CI, or partially by -CN or -NO ₂ , with the proviso that not all R ² and R ¹ are fully halogenated,
00			and where one or two carbon atoms of the R ¹ and/or R ² may be
30			replaced by heteroatoms and/or atomic groups selected from the group -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO ₂ -, -SO ₂ O-, -N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially or perfluorinated C ₁ - to C ₆ -alkyl or -C ₆ F ₅ , where the α -position of the R ¹ is not replaced for X = O, S.
35	12.	Process fo	or the preparation of salts according to one of Claims 8 or 9,

12. Process for the preparation of salts according to one of Claims 8 or 9, characterised in that an alkali metal fluoride of the general formula DF, where

D selected from the group of the alkali metals, is reacted in a polar organic solvent with

$$R^FSO_2N(CF_3)_2$$
 or $R^FC(O)N(CF_3)_2$

where $R^F = F$ or C_pF_{2p+1} , where p = 1 - 8,

5 and a salt of the general formula (5)

$$\begin{bmatrix} A'' & & & \\ (R^1)_n - X & & & \\ & & & \end{bmatrix}^{2+}$$

$$(5)$$

where

E- =

F⁻, Cl⁻, Br⁻, I⁻, BF₄⁻, ClO₄⁻, AsF₆⁻, SbF₆⁻, SbCl₆⁻, PF₆⁻, R^FSO₃⁻, FSO₃⁻, (R^F)₂P(O)O⁻, R^FP(O)₂O⁻, RSO₃⁻, ROSO₃⁻, $\frac{1}{2}$ SO₃²⁻, CN⁻, SCN⁻, R^FC(O)O⁻, RC(O)O⁻, 2,4-dinitrophenolate or 2,4,6-trinitrophenolate, where R^F is a perfluorinated C₁ to C₈-alkyl group or perfluorinated aryl group and R is a C₁ to C₈-alkyl group or aryl group

10

X, Y = each, independently of one another, N, P, O or S

15

n, m = an integer selected from 0, 1 or 2 in such a way that X, Y are each saturated in accordance with their valency increased by 1,

20

A", B" = saturated, partially or fully unsaturated 0- to 4-membered hydrocarbon chain,

in which the carbon atoms may be replaced by identical or different heteroatoms selected from N, P, O and S,

where at least one carbon atom is present in the chains A" and B" together and

25

where the carbon atoms of the hydrocarbon chains A" and B" and the heteroatoms present therein are saturated by substituents R² in accordance with their valency,

	R^1 , R^2 , $R^3 =$	-H, with the proviso that there is no bond to the positively charged heteroatom,
_		straight-chain or branched alkyl having 1-20 carbon atoms
5		straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds
		straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds
		saturated, partially or fully unsaturated cycloalkyl having 3-7
10		carbon atoms
		halogen, in particular fluorine or chlorine, with the proviso that, for X, = N, O, S, there is no halogen-heteroatom bond,
		halogen, in particular fluorine or chlorine, with the proviso that there is no halogen-heteroatom bond,
15		-NO ₂ , with the proviso that there is no bond to a positively
		charged heteroatom,
		-CN, with the proviso that there is no bond to a positively charged heteroatom,
20		where the R ¹ , R ² and/or R ³ in different and/or identical position
		of the heterocyclic ring are in each case identical or different,
		where the R ¹ , R ² and/or R ³ may be connected to one another in
25		pairs by a single or double bond,
		where one or more R ¹ , R ² and/or R ³ may be partially or fully
		substituted by halogens, in particular -F and/or -Cl, or partially
		by -CN or -NO ₂ , with the proviso that not all R^1 , R^2 and R^3 are
		fully halogenated,
30		D1 D2
		and where one or two carbon atoms of the R ¹ , R ² and/or R ³ may be replaced by heteroatoms and/or atomic groups selected
		from the group -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO ₂ -, -SO ₂ O-,
		-N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially
35		or perfluorinated C_1 - to C_6 -alkyl or $-C_6F_5$, where the α -position of the R^1 is not replaced for $X = O$, S ,

where the heterocyclic di-cation is a 4-, 5-, 6-, 7-, 8- or 9-membered ring.

- 13. Process according to Claim 11 or 12, characterised in that the alkali metal fluoride employed is KF or RbF.
- 5 14. Process according to one of Claims 11 to 13, characterised in that the reaction takes place at temperatures between -40°C and 80°C, in particular at 0°C to 40°C.
- 15. Process according to one of Claims 11 to 14,
 characterised in that the reaction takes place in a polar organic
 solvent selected from the group acetonitrile, dimethoxyethane, dimethylformamide and propionitrile.
 - 16. Process according to one of Claims 11 to 15, characterised in that the reaction is carried out as a one-pot reaction.
- 15 17. Process according to one of Claims 11 to 16, characterised in that the reaction for E⁻ = F⁻ is carried out without added alkali metal fluoride DF.
- 18. Process according to one of Claims 11 to 17,
 characterised in that the starting materials for the reaction are
 employed in approximately equimolar ratio to one another.
 - 19. Use of a salt according to one of Claims 1 to 10 as ionic liquid.
 - 20. Use of a salt according to one of Claims 1 to 10 as non-aqueous electrolyte.
 - 21. Use of a salt according to one of Claims 1 to 10 as reagent for the introduction of N(CF₃)₂ groups.
- 25 22. Use of a salt according to one of Claims 1 to 10 as phase-transfer catalyst.

23. Use of a salt according to one of Claims 1 to 10 as intermediate for the synthesis of liquid-crystal compounds or active ingredients, in particular for medicaments or crop-protection agents.